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Crystallization of Polymers from Solution under Shearing Stress

I Polyethylene

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Synopsis

We tried to clarify the crystallization mechanism of long chain polymers in solution under shearing stress using polyethylene. From the bright and dark field electron microscope observations and the electron diffraction study, we demonstrated that the resulting fibrous crystals consist of the central threads with an extended chain character and the lamellae with a folded chain character nucleated on the threads. The measurements of thermal and mechanical properties gave the additional confirmation for this suggestion. From these results we discussed the crystallization mechanism on the fibrous crystals.

§ 1. Introduction

Polymer crystals are classified into two categories from the view of their crystal habits; namely lamellar crystals and fibrous ones.

The crystallization of polymers from dilute solution usually results lamellar crystals in which long chain molecules are folded back and forth with relatively short period (100A). This chain folding, therefore, proceeds intramolecularly. Polymer crystals obtained from more concentrated solution or melt have more complicatedly polycrystalline morphology, but the individual crystallites are essentially composed of folded chain lamellae. The fraction of chain folding and the role played by intramolecular crystallization in these crystals is not so ideal as those of single crystals from dilute solution, and the crystal growth is assumed to occur by complicated screw dislocation mechanism.

On the other hand, another type of polymer crystals is the fibrous crystals, and is observed in the native state of natural polymers, such as the fibrous proteins and in the fiber state of synthetic polymers stretched. These fibrous crystals are characterized by a preferred fibrous crystalline orientation in which long chain molecules are packed side by side, by the intermolecular crystallization. A limiting structural model of the fibrous crystals is a traditional fringed micelle model. If the chain folding is intrinsic property of polymer molecules on crystallization, this model based on intermolecular crystallization seems to be unreasonable at least in the absence of stress. A few years ago, Kobayashi[1] illustrated schematically the intermolecular crystallization process to form fibrous crystals, by drawing out polymer molecules from lamellar crystals. Some of unsolved problems have been left for this deformation mechanism under stress.

It has been well known that the crystallization from melt under stress gives a preferred oriented texture; this behavior has been often observed in the process of molding, extruding and spinning of polymer substances which has technological importance, but their crystallization mechanism has not been clarified completely. Keller and Machin[2] have suggested that these oriented textures are resulted from fibrous primary nucleus due to oriented chains formed in the melt by mechanical forces. Williamson[3] showed intercrystalline links as the result of the crystallization under stress using the techniques of Keith and Padden,[4] and demonstrated the feature of this type of growth. This fact indicates that polymer chains may be intermolecularly condensed in

the form of fiber.

Pennings and Kiel[5] found that if the moderately concentrated solution of polyethylene are mechanically agitated by stirring upon cooling, fibrous crystals are obtained. They pointed out that the fibrous backbones of these crystals are essentially of an extended chain character. Keller and Machin[2] supported this suggestion from the subsequent similar experiment and assumed the two components crystallization in the form of extended molecules and chain folded lamellae. Thus, they presented a working hypothesis which the row nucleation is the basic process of crystallization under stress or during flow. Observing the peculiar deformation process of the piled-up lamellar texture in extruded polyethylene film, Kobayashi[6] speculated that the fibrous crystals prepared from solution under stress are also the results of spiral growth of lamellae along fiber axis. Kawai[7] suggested also that the influence of shearing stress to molecules in solution makes nucleation easier and the fibrous crystal habit is formed by the subsequent mechanical deformation of lamellar crystals.

In order to elucidate in more detail the morphology and structure of the fibrous crystals, we studied also on the crystallization from polyethylene solutions under shearing stress, with more variations of crystallization condition. As the results, we tried to clarify the crystallization mechanism of long chain polymers from solutions under shearing stress.

§ 2. Experiment

Materials and Solvents

The polymer used in this study was linear polyethylene (Marlex 6009, The Phillips Petroleum Company). The solvents used were xylene as a good solvent and octadecane as a poor solvent.

Crystallization Procedures

Solution of the polymer was prepared in a tube (diameter 30 mm) from the sample with xylene or octadecane as the solvent at concentrations of 0.01% to 5% (by weight) by heating the polymer solvent mixtures at 130°C to 138°C for 30 min. and it was transferred to an oil bath which had been kept to the desired temperature. It was then stirred at the desired conditions of stirring (800 to 5000 rpm) with a stirrer (diameter 6 mm). Crystallization occurred at solution in the form of ring fiber and the fiber clustered on the stirrer. When a few percent of the polymer was recovered, the stirrer was transferred to pure solvent of the same temperature and the materials deposited by subsequently crystallization were washed out for about 1 hr. Thus, we obtained the film-like products on the stirrer.

Preparation of Specimens for Electron Microscopy

When very small amounts of the polymer were deposited on the stirrer, crystallization was stopped. The stirrer with the crystals was covered with the acetyl cellulose film immersed in acetone and when the acetyl cellulose film dried into a tough film, it was stripped from the stirrer, taking the crystals with it. The acetyl cellulose film with the crystals contained on one side was covered with a thin film of carbon. Pieces of the film were placed on 150 mesh microscope grids and the acetyl cellulose was dissolved away in acetone, leaving the carbon film containing the crystals to place on the grids. The crystals on the film of carbon supported by the grids then were shadowed with Pt-Pd for morphological observations.

Electron Microscopy

A Hitachi HU-11B was used for all of the microscopy described in this paper. Diffraction patterns were calibrated with the Debye-Scherrer rings from the Platinum.

X-ray Diffraction Study

X-ray diffraction photographs for the resulting film were obtained in a flat camera with the use of nickel-filtered CuKα radiation.

Thermal Analysis

A Perkin-Elmer Differential Scanning Calorimeter was used. The temperature scale was calibrated by the onset of the melting of Indium at 429°K, heated at the same rate as the sample.

§ 3. Results and Discussion

Experimental results shown below are confined to the fibrous crystals deposited on the stirrer.

Morphology

It was observed with a polarizing microscope that the film obtained from solution under shearing stress possesses remarkable macroscopic oriented texture to the stress direction. Figure 1 shows a wide angle x-ray diffraction

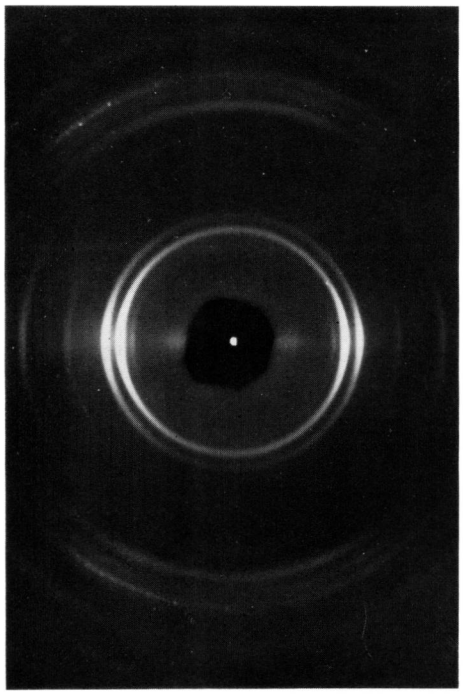

Fig. 1 Wide angle x-ray diffraction pattern of polyethylene film obtained from solution under shearing stress, with the beam perpendicular to the film whose oriented direction was directed along the meridian.

pattern with the beam perpendicular to the film whose oriented direction was directed along the meridian. From this pattern the fiber axis can be confirmed to be parallel to the stress direction.

Electron micrograph of typical fibrous crystals is shown in Figure 2 which are crystallized from a 3% solution of polyethylene in octadecane at 130°C. The crystal have revealed fine fibrous nature with 500A in width and they have regular transversal cross banded structure on the central threads. Electron diffraction pattern from a bundle of fibrous crystals gives well defined fiber pattern as shown in Figure 3. This pattern indicates that the molecular chains are oriented along the fiber direction. This fact is not conflicted with the morphological observation that the fibrous crystals consist of the two component systems of extended chain fibers and folded chain lamellae.

To clarify the justification of the two component systems, we carried out dark field image observations. Figures 4 and 5 show the dark field micrographs corresponding to the composite (110) and (200) illuminations and the (002) one, respectively. We can conclude

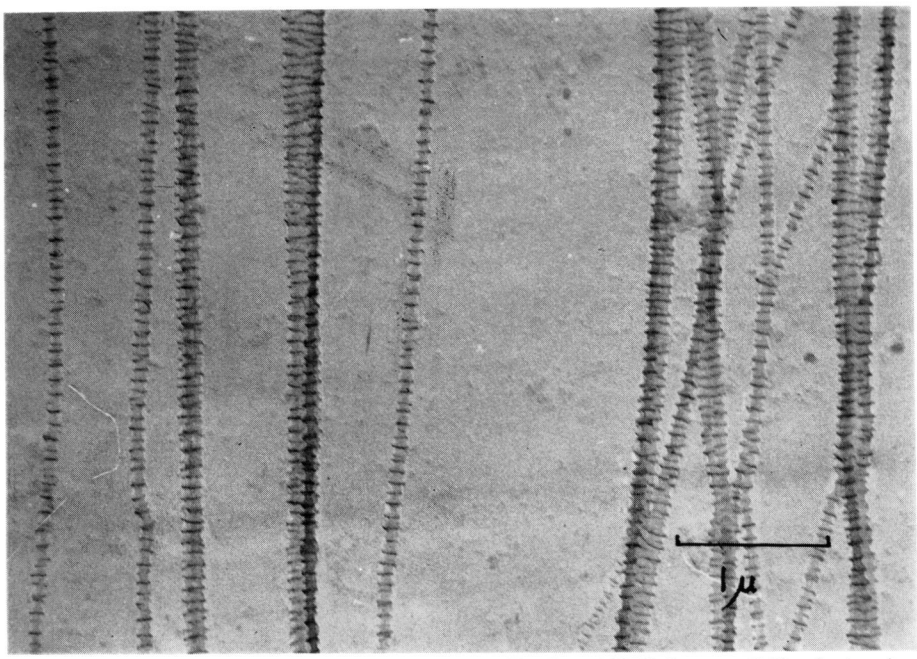

Fig. 2 Electron micrograph of polyethylene crystallized at 130°C from a 3% solution in octadecane under shearing stress. It shows that the crystals have fine fibrous nature with 500 A in width and regular transversal cross banded structure on the central threads.

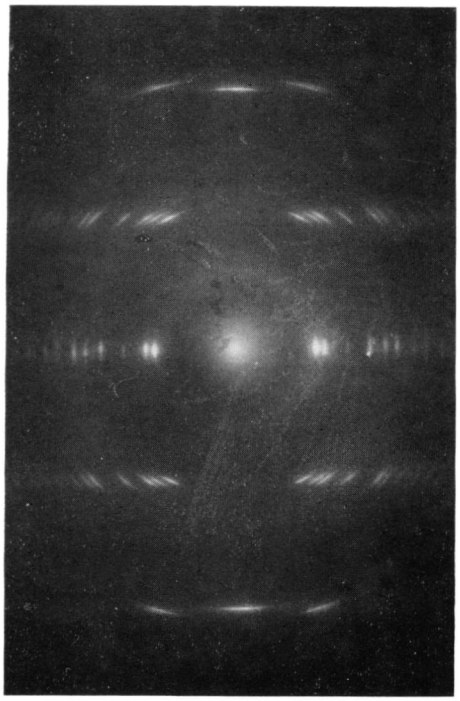

Fig. 3 Electron diffraction pattern from the fibrous crystals of polyethylene. Sample was prepared with the same crystallization condition as that in Fig. 2. This pattern indicates well defined fiber pattern.

that bright striations in the composite (110) and (200) dark field micrograph result mainly from the deposited lamellae, because they are aligned transversally to the fiber axes and located near the outer side of the central threads. On the other hand, the (002) dark field illumination originates from the central threads as well the lamellae and the striations from the central threads are longer than those of lamellae. These features of dark field micrographs strongly support the existence of central threads in the fibrous crystals. We shall conclude experimentally that the fibrous crystals are composed of the two component systems of extended chain fibers and folded chain lamellae as originally suggested by Pennings and Kiel.[5]

The Crystallization Conditions

The morphology of the fibrous crystals strongly depends upon the crystallization conditions, such as crystallization temperature, rate of shearing stress, viscosity of solution, polymer concentration and molecular weight of the polymer.

Pennings and Kiel[5] chose the relatively higher crystallization temperature of 102°C at the first time when the fibrous crystals were prepared from a 5% solution of polyethylene

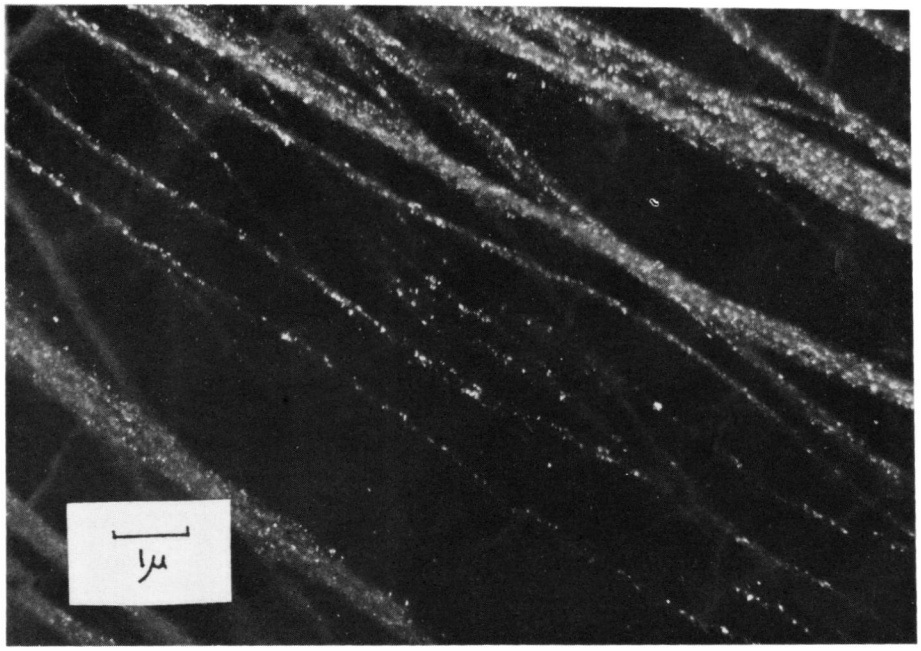

Fig. 4 Dark field micrograph of the composite (110) and (200) illumination. Sample was prepared at 105°C from a 2.5% solution in xylene. We find that bright striations result mainly from the deposited lamella on the central threads.

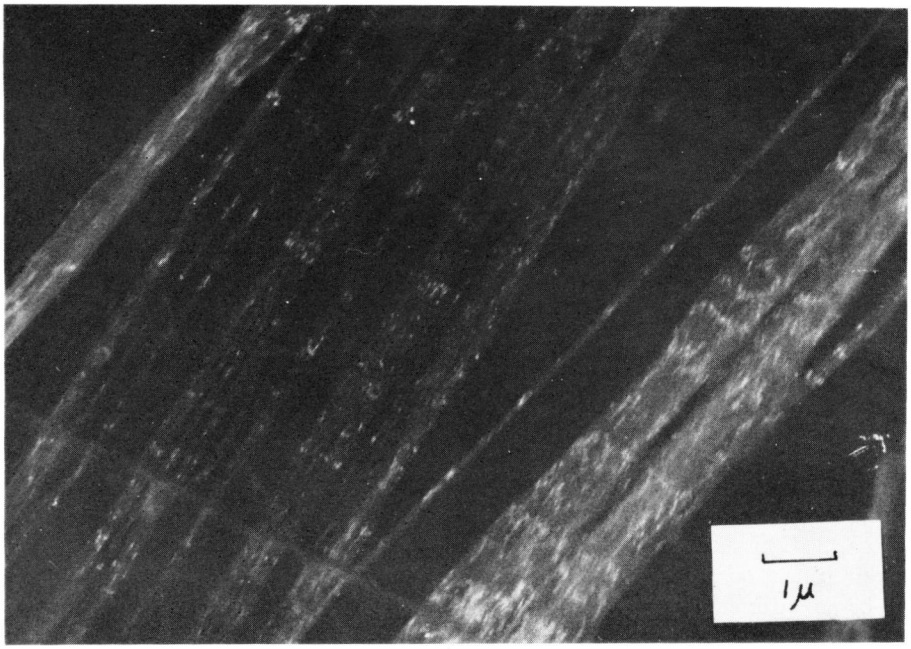

Fig. 5 Dark field micrograph of the (002) illumination. Sample was prepared with the same crystallization condition as that in Fig. 4. We find that bright longer striations result form the central threads.

in xylene under shearing stress. In the absence of stress polyethylene molecules fail to crystallize from the same solution at the same temperature. As we wish to manifest from the morphological observations whether the crystallization mechanism is same or not in the case of the presence and absence of stress, hence it is desirable to choose the higher crystallization temperature at which the polymer molecules can not crystallize in the absence of stress. From this point of view, the crystallization temperature used by Kawai[7] is seemed to be

Fig. 6 Electron micrograph of polyethylene crystallized at 89°C from a 0.1% solution in xylene. It shows that the lamellar crystallization is greatly enhanced.

too low. We obtained the fibrous crystals at very high crystallization temperature of 130°C from the solution of octadecane in which the precipitating temperature of polyethylene is 102°C in the absence of stress. The resulting morphology has been shown in Fignre 2.

We consider next the effects of the polymer concentrations. At the concentrations lower than 0.1%, the effect of shearing stress to polymer chains are thought to be decreased largely. In fact, a 0.1% solution of polyethylene in xylene stirred with 800 rpm results lamellar crystals as shown in Figure 6.

The degree of polymerization is one of the important requisites to obtain the fibrous crystals. When low molecular weight polyethylene was used, we could not obtain the fibrous crystals. This fact is interesting in concerning with the spinability and the entanglement of polymer chains.

Thermal and Mechanical Properties of Fibrous Crystals

Physical properties of the fibrous crystals should reflect their morphology.

In previous section we concluded that the fibrous crystals are the two component systems consisting of extended chain fibers induced by the stress and folded chain lamellae nucleated on the fibers. To confirm this conclusion, we investigated thermal properties of the fibrous crystals with a differential scanning calorimeter at a heating rate of 10°C/min. Figure 7 shows a typical DSC curve of the crystals which were prepared at 105°C from a 3% solution in xylene. This melting peak of 135°C is lower than that of highly crystallized materials from melt but much higher than that of single crystals from dilute solution. The apparent heat of fusion was found to be 55 cal/g comparable with that of single crystals prepared at 85°C. The most remarkable feature is that this sample has a small amount of highly superheatable materials. The range of superheating extends up to 150°C. From these results we suggest that the superheatable portion corresponds to the extended chain backbone in fibrous crystals. Wunderlich et al.[8] have recently reported the similar results on the fibrous crystals prepared at 95°C from a 1% solution of polyethylene in xylene. We believe that the crystals prepared at high crystallization temperature under high shearing stress will probably give a larger amount of highly superheatable portions.

Preliminarily we obtained the stress-strain curves on the film of fibrous crystals which are prepared at 105°C from a 3% solution of polyethylene in xylene with an Instron-type extensometer. The value of tensile strengths at break of 20% are very high and the calculated Young's modulus from the stress-strain curve is 2.3×10^4 kg/cm^2 comparable with that of highly elongated melt crystallized polyethylene. These results also support that the backbones of these fibrous crystals consist of extended chains.

The Crystallization Mechanism

From the bright and dark field electron microscope observations and the electron diffraction study, we demonstrated that the fibrous crystals consist of the central threads with an extended chain character and the

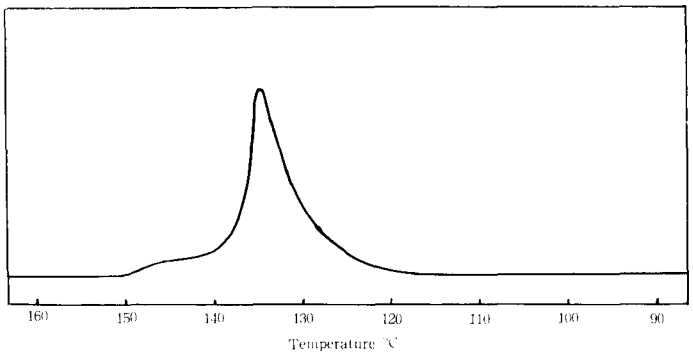

Fig. 7 Representative DSC thermogram for the fibrous crystals of polyethylene which is obtained at 105°C from a 3% solution in xylene; Heating rate is 10°C/min. The remarkable feature is that this sample has a small amount of highly superheatable materials. The range of superheating extends up to 150°C.

lamellae with a folded chain character nucleated on the threads. Furthermore, the measurements of thermal and mechanical properties gave the additional confirmation for the two component structural model.

Now, it is necessary to consider the nucleation mechanism for the formation of the central threads. As the polymer molecules in solution have the ability to sustein the deformation, the alignment of molecules are assumed to occur by shearing forces.

Furthermore the chain entanglement may accelerate such alignment. The configurational entropy is decreased by the deformation of polymer chain under stress and the entropy change to the crystalline state becomes small to be favorable for crystallization of long chain polymers. The orientation induced by shearing force is presumed to enhance the formation of intermolecular nuclei.

Thus, the central threads observed in fibrous crystals can be formed and these provide a substrate upon which other molecules may readily condense by chain folding. The increase of crystallization rate in solution is due to this fibrous primary nucleus.

It should be noted that this crystallization mechanism has a question whether the ideal alignment of molecules can occur in solution under shearing stress. This problem will be solved in due course by obtaining the informations on the molecular conformations in solution under stress.

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